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(54) **PRODUCTION OF ACRYLIC ACID**

(56) **References Cited**

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FOREIGN PATENT DOCUMENTS

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EP	2495233	9/2012
WO	0116346	3/2001
WO	2011063363	5/2011

(73) Assignee: **Shell Oil Company**, Houston, TX (US)

OTHER PUBLICATIONS

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(58) **Field of Classification Search**

CPC **C07C 51/16**; **C07C 51/377**

USPC **562/532**, **599**

See application file for complete search history.

Bettahar, M.M., et al.: "On the partial oxidation of propane and propene on mixed metal oxide Catalysts"; Applied Catalysis A: General; vol. 145; pp. 1-48; 1996.

Pina, Christina Della et al.: A green approach to chemical building blocks. The case of 3-hydroxypropanoic acid; Green Chemistry; vol. 13, No. 7; p. 1624, XP055059820.

Ruppert, Agnieszka M. et al.: "Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals"; Angew. Chem. Int. Ed.; vol. 51; pp. 2564-2601; 2012.

Li et al.; Journal of Catalysis; vol. 270; pp. 48-59.

Shen, Yihong, et al.: "Efficient synthesis of lactic acid by aerob oxidation of glycerol on Au—Pt/TiO₂ catalysts"; Chemistry—A European Journal, Wiley-VCH Verlag GmbH & Co., KGAA, Weinheim, DE, vol. 16, No. 25; pp. 7368-7371; XP009146561.

Prati, L., et al.: Gold on Carbon as a new catalyst for selective liquid phase oxidation of diols; Journal of Catalysis, Academic Press, vol. 176, No. 2, Jun. 10, 1998, pp. 552-560, XP004447366.

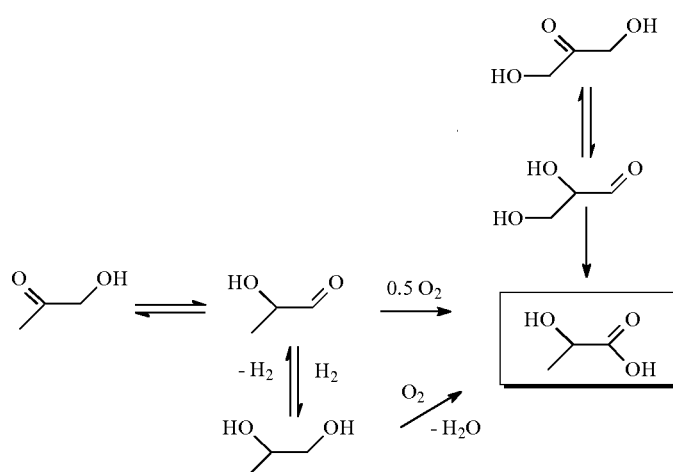
Nikolaos, Dimitratos, et al.: Selective formation of lactate by oxidation of 1,2-propanediol using gold palladium alloy supported nanocrystals, Green Chemistry; Royal Society of Chemistry; vol. 11, No. 8; pp. 1209-1216; Aug. 2009, XP008137932.

Primary Examiner — Sikarl Witherspoon

(57) **ABSTRACT**

The invention relates to a process for producing acrylic acid, comprising: converting a C3-oxygenate into a C3-hydroxyacid, wherein said C3-oxygenate is selected from the group consisting of 1-propanol, 2-propanol, propanal, acetone, monopropylene glycol, monohydroxyacetone, 2-hydroxypropanal, dihydroxyacetone and 2,3-dihydroxypropanal; and converting the C3-hydroxyacid into acrylic acid.

8 Claims, 1 Drawing Sheet



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PRODUCTION OF ACRYLIC ACID

PRIORITY CLAIM

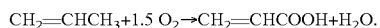
The present application is the National Stage (§371) of International Application No. PCT/EP2014/050181, filed Jan. 8, 2014, which claims priority from European Application No. 13150517.4, filed Jan. 8, 2013 incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to a process for producing acrylic acid.

BACKGROUND OF THE INVENTION

Acrylic acid is a chemical for which the worldwide demand is high, about 5 Mt/a (million ton per annum) in 2008 and possibly about 9 Mt/a by 2025. A known route for the production of acrylic acid comprises the oxidation of propene into acrolein (propenal) and then oxidation of the acrolein into acrylic acid. See for example "On the partial oxidation of propane and propene on mixed metal oxide catalysts" by M. M. Bettahar et al. in *Applied Catalysis A: General*, 145, 1996, p. 1-48. The overall reaction stoichiometry for this route is as follows:



A disadvantage of the above-mentioned route for the production of acrylic acid is that two oxygen atoms have to be introduced into the propene by the use of an oxygen containing gas at high temperature (about 350° C.) and with release of a large amount of heat (about 600 kJ/mol). A further disadvantage is that propene has to be used which may be derived from propane. Both propene and propane are currently only readily available as fossil feedstocks and are therefore not renewable.

WO 2011/063363 discloses the conversion of malonate semialdehyde to 3-hydroxypropionic acid (3-HPA) and the subsequent conversion of the 3-HPA to acrylic acid.

WO 01/16346 describes a process for producing 3-HPA from glycerol by fermentation. The 3-HPA may then be converted into acrylic acid.

EP 2495233 describes a process in which acrylic acid may be derived from biomass-derived lactic acid.

Cristina Della Pina et al., *Green Chemistry*, 2011, 13(7), 1624 discloses a synthesis of acrylic acid from 3-HPA and several routes to produce 3-HPA, with starting materials including 1,3-propanediol, propionic acid and glycerol.

In addition to acrylic acid, monoethylene glycol is also a chemical for which the worldwide demand is high, about 20 Mt/a (million ton per annum) in 2008. Monoethylene glycol may be advantageously produced from sugar sources, such as sucrose, glucose, xylose or fructose and the corresponding polysaccharides, cellulose, hemicellulose, starch and inulin. A disadvantage of this route is that in addition to monoethylene glycol, also a lot of monopropylene glycol is formed. It may even be the case that two to three times more monopropylene glycol is formed than monoethylene glycol. See for example "Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals" by Agnieszka M. Ruppert et al. in *Angew. Chem. Int. Ed.*, 2012, 51, p. 2564-2601.

In contrast to acrylic acid and monoethylene glycol, the worldwide demand for monopropylene glycol is not high, about 1.5 Mt/a (million ton per annum) in 2008. Currently, it

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is estimated that the worldwide demand for monoethylene glycol is ten times higher than that for monopropylene glycol. Because of this lower demand for monopropylene glycol, processes for converting sugar sources into monoethylene glycol may not be commercialized, unless the selectivity to monoethylene glycol would be drastically increased. Such selectivity increase is difficult to achieve. Consequently, there is currently a need in the art to valorize the monopropylene glycol that is automatically formed when transforming sugar sources into monoethylene glycol. A desired valorization could be an application wherein the monopropylene glycol is converted into a chemical for which the worldwide demand is high.

The above-mentioned monopropylene glycol is just one example of a C3-oxygenate. C3-oxygenates contain 3 carbon atoms and 1 or more oxygen atoms. There are also C3-oxygenates other than monopropylene glycol, which may contain 1, 2 or 3 oxygen atoms and which may also be formed as undesired (by)products in certain production processes such as biomass conversion processes. Such biomass conversion process may be the aqueous phase reforming of sugars, as disclosed by N. Li et al. in *Journal of Catalysis*, 2010, 270, p. 48-59. Examples of such other C3-oxygenates include: 1-propanol, 2-propanol, propanal, acetone, monohydroxyacetone, 2-hydroxypropanal, dihydroxyacetone and 2,3-dihydroxypropanal.

Consequently, there is a need in the art to valorize C3-oxygenates in general, such as for example monopropylene glycol, which may be formed as undesired (by)products in certain production processes such as biomass conversion processes.

SUMMARY OF THE INVENTION

Surprisingly, it was found that the above-mentioned C3-oxygenates can be valorized by using them in a process for producing acrylic acid, by first converting them into a C3-hydroxyacid and then converting the C3-hydroxyacid into acrylic acid. Advantageously, in such way, the C3-oxygenate is converted into a chemical for which the worldwide demand is high, namely acrylic acid. Further, advantageously, in such way, acrylic acid may be produced from a renewable feedstock since the starting C3-oxygenates may originate from biomass conversion processes. Further advantages of the present invention appear from the detailed description below.

Accordingly, the present invention relates to a process for producing acrylic acid, comprising:

converting a C3-oxygenate into a C3-hydroxyacid, wherein said C3-oxygenate is selected from the group consisting of 1-propanol, 2-propanol, propanal, acetone, monopropylene glycol, monohydroxyacetone, 2-hydroxypropanal, dihydroxyacetone and 2,3-dihydroxypropanal; and converting the C3-hydroxyacid into acrylic acid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a number of preparation routes starting from C3-oxygenates and resulting in a C3-hydroxyacid.

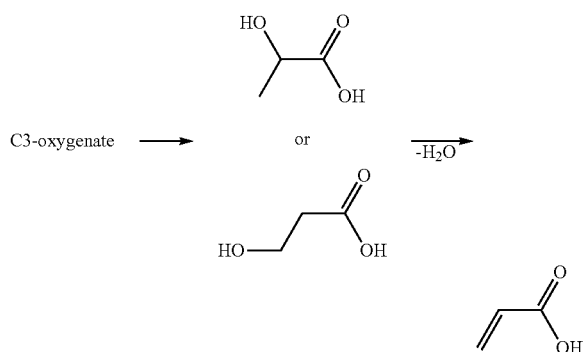
DETAILED DESCRIPTION OF THE INVENTION

In the present invention, a C3-oxygenate is converted into acrylic acid via a C3-hydroxyacid as an intermediate. Said C3-hydroxyacid contains 3 carbon atoms and 3 oxygen atoms in the form of a hydroxyl group and a carboxyl group. The other atoms in such C3-hydroxyacid are hydrogen atoms.

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Said C3-hydroxyacid is preferably a C3-monohydroxyacid (containing only one hydroxyl group). More preferably, said C3-hydroxyacid is lactic acid (2-hydroxypropanoic acid).

In the final step of the present process, such C3-hydroxyacid is dehydrated into acrylic acid. The present process is illustrated in the following general reaction scheme wherein the starting material for the last step of the process is a C3-hydroxyacid:



In the present process, the starting material is a C3-oxygenate. Within the present specification, a C3-oxygenate means a compound which contains 3 carbon atoms and 1, 2 or 3 oxygen atoms. The other atoms in such C3-oxygenate are hydrogen atoms. In the present process, the C3-oxygenate is not a C3-hydroxyacid, because by C3-oxygenate reference is made herein only to the starting material of the present process.

Examples of C3-oxygenates containing 1 oxygen atom which may suitably be used in the present invention are 1-propanol, 2-propanol, propanal and acetone.

Examples of C3-oxygenates containing 2 oxygen atoms which may suitably be used in the present invention are monopropylene glycol, monohydroxyacetone and 2-hydroxypropanal.

Examples of C3-oxygenates containing 3 oxygen atoms which may suitably be used in the present invention are dihydroxyacetone and 2,3-dihydroxypropanal (glyceraldehyde).

Preferably, in the present process, the C3-oxygenate contains 2 oxygen atoms. More preferably, such C3-oxygenate containing 2 oxygen atoms is monopropylene glycol, monohydroxyacetone, 2-hydroxypropanal, most preferably monopropylene glycol.

As discussed above, a disadvantage of the route for the production of acrylic acid by oxidation of propene is that two oxygen atoms have to be introduced into the propene by the use of an oxygen containing gas at high temperature (about 350° C.) and with release of a large amount of heat (about 600 kJ/mol). A further disadvantage is that propene has to be used which may be derived from propane, which are both fossil feedstocks and are therefore not renewable.

Surprisingly, with the integrated process of the present invention the above-mentioned disadvantages are avoided, while at the same time, advantageously, by means of the present invention C3-oxygenates, such as for example monopropylene glycol, which may be formed as undesired (by) products in certain production processes such as biomass conversion processes, as discussed above, are valorized by transforming them into a chemical for which the worldwide demand is indeed high, namely acrylic acid.

In addition, it has appeared that the present process for the production of acrylic acid has a relatively high route effi-

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ciency, also when compared to other acrylic acid production routes using renewable feedstocks, which will now be further explained.

In the present process, acrylic acid is made from a C3-oxygenate which may be obtained from a renewable feedstock. That is, in the present process, acrylic acid is not made from propene that would normally originate from a non-renewable, fossil feedstock. As an alternative, acrylic acid could also be made from propene produced from a renewable feedstock. For example, propene could be produced from a sugar source, which is a renewable feedstock, after which the propene is oxidized into acrylic acid using conventional technologies as already discussed above. The present inventor, however, has found that such an alternative route using a renewable feedstock for providing propene would not be the most efficient route in terms of mass efficiency, carbon efficiency and/or fossil CO₂ intensity (or fossil CO₂ footprint).

The most efficient route for the production of acrylic acid would be one having effective H/C ratios (H/C_{eff}) which is as close to zero as possible for all compounds involved in the production route. H/C_{eff} is defined as follows, based on the carbon content (C), hydrogen content (H) and oxygen content (O) of the compound in question (all expressed in atom %):

$$H/C_{eff} = (H - 2 \cdot O) / C.$$

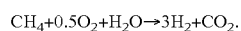
For illustration purposes, this definition when applied to CH₄ results in H/C_{eff}=4. When applied to CO₂, it results in the opposite: H/C_{eff}=-4. It was surprisingly noticed that both sugars (e.g. glucose) and acrylic acid have H/C_{eff}=0. In contrast, propene is characterized by H/C_{eff}=2. On the other hand, C3-oxygenates are favourably characterised by a H/C_{eff} which is closer to zero and represent therefore a more efficient feedstock for or intermediate in the production of acrylic acid.

H/C_{eff} values for some C3-oxygenates and the H/C_{eff} values for methane (CH₄), carbon dioxide (CO₂), sugars (e.g. glucose), acrylic acid and propene are mentioned in the table below.

Compound	H/C _{eff}
methane	4
propene	2
1- or 2-propanol	2
acetone, propanal, monopropylene glycol, 1,3-dihydroxypropane	1.33
glycerol, monohydroxyacetone, 1- or 2-hydroxypropanal	0.67
acrolein	0.67
propanoic acid	0.67
sugars (e.g. glucose)	0
dihydroxyacetone, dihydroxypropanal	0
2- or 3-hydroxypropanoic acid	0
acrylic acid	0
carbon dioxide	-4

H/C_{eff} means effective H/C ratio, as defined above.

This surprising finding can be demonstrated by means of the following calculations for different routes all using glucose as common feedstock and acrylic acid as common product. All individual reactions steps were considered and added to one another to develop the overall reaction equations, assuming 100% molar selectivity. The hydrogen needed for hydrogenation reactions is assumed to come from partial oxidation of methane with the following reaction stoichiometry:

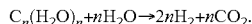


Therefore, the use of hydrogen obtained from methane in the above way results in the emission of CO₂ the carbon of

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which CO₂ originates from a fossil feedstock (i.e. methane). Such CO₂ is herein referred to as “fossil CO₂”.

Such emission of fossil CO₂ could be avoided by producing hydrogen from a renewable feedstock, such as a sugar source (e.g. glucose), with the following overall reaction stoichiometry:



However, the gain achieved by the reduction of fossil CO₂ emissions would then be more than offset by additional losses in mass efficiency and carbon efficiency which would result in increased feedstock consumption, as illustrated by the above overall reaction stoichiometry.

In the table below, the overall mass efficiency, carbon efficiency and fossil CO₂ intensity are mentioned for the acrylic acid production route of the present invention and for a comparative acrylic acid production route wherein the acrylic acid is produced by oxidation of propene which propene is obtained from converting a sugar source. The overall mass efficiency, carbon efficiency and fossil CO₂ intensity for each route were calculated as follows:

Overall mass efficiency (wt. %; hereinafter “ME”)=
[(mass of acrylic acid)/(total mass of feed)]*100

Overall carbon efficiency (C %; hereinafter “CE”)=
[(carbon in acrylic acid)/(total carbon in feed)]
*100

Overall fossil CO₂ intensity (C %; hereinafter “FCI”)=
[(carbon from CH₄)/(carbon in acrylic acid)]
*100.

In general, it is preferred to have an overall mass efficiency and overall carbon efficiency which are as high as possible, in combination with an overall fossil CO₂ intensity which is as low as possible.

	H/C _{eff}	ME (wt. %)	CE (C %)	FCI (C %)
Route via propene (comparison): step 1: glucose hydrogenolysis → 1- or 2-propanol step 2: 1- or 2-propanol dehydration → propene step 3: propene oxidation → acrylic acid Overall: C ₆ H ₁₂ O ₆ + 4O ₂ + 2CH ₄ → 2C ₂ H ₃ COOH + 6H ₂ O + 2CO ₂	2	42	75	33
Route via a C3-hydroxyacid: step 1: glucose cleavage → dihydroxyacetone, dihydroxypropanal step 2: dihydroxyacetone, dihydroxypropanal rearrangement → lactic acid step 3: lactic acid dehydration → acrylic acid Overall: C ₆ H ₁₂ O ₆ → 2C ₂ H ₃ COOH + 2H ₂ O	0	80	100	0

H/C_{eff} means effective H/C ratio, as defined above.

The mentioned value for H/C_{eff} is the one for the least favourable compound, i.e. having the highest H/C_{eff}, from the whole route in question. All routes both start and end with H/C_{eff}=0, for glucose and acrylic acid, respectively.

ME, CE and FCI mean overall mass efficiency, overall carbon efficiency and overall fossil CO₂ intensity, respectively, as defined above.

In conclusion, the above calculations confirm that surprisingly the acrylic acid production process of the present inven-

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tion, which starts from C3-oxygenates which have a favourable H/C_{eff} and which may be obtained from a sugar source (e.g. glucose) which is a renewable feedstock, has a higher route efficiency, in terms of a combination of a higher overall mass efficiency, a higher overall carbon efficiency and a lower overall fossil CO₂ intensity, when compared to routes that proceed via propene obtained from glucose as a renewable feedstock. Therefore, advantageously, in addition to valorizing C3-oxygenates formed as undesired (by)products in certain production processes, such as biomass conversion processes, by transforming them into acrylic acid, by means of the present integrated process for the production of acrylic acid, surprisingly, also a high route efficiency is coupled to the use of renewable feedstocks.

Preferably, in the present invention, the C3-oxygenates, for example monopropylene glycol, originate from converting a renewable feedstock into such C3-oxygenates.

In the present invention, the C3-oxygenates, for example monopropylene glycol, may originate from converting sugar sources, a renewable feedstock, such as sucrose, glucose, xylose or fructose, into such C3-oxygenates, for example by means of hydrogenolysis or hydrocracking of such sugar sources. These sugars may be used alone or in admixture. Further, these sugars may be present in monomeric, dimeric or polymeric form. Suitable polymeric sugars are cellulose, starch, inulin and hemicellulose.

For example, monoethylene glycol and monopropylene glycol may be produced by the hydrogenolysis of one or more of the above-mentioned sugar sources. After separating the monopropylene glycol from the monoethylene glycol, the monopropylene glycol may advantageously be used as the C3-oxygenate in the present process. Such hydrogenolysis of sugar sources may be performed in any way, for example as described in above-mentioned “Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals” by Agnieszka M. Ruppert et al. in Angew. Chem. Int. Ed., 2012, 51, p. 2564-2601. Further reference is made to the above-mentioned disclosure of aqueous phase reforming of sugars by N. Li et al. in Journal of Catalysis, 2010, 270, p. 48-59. The disclosures of these publications are incorporated herein by reference.

In the present process wherein acrylic acid is produced and wherein a C3-hydroxyacid is an intermediate that is converted into acrylic acid, the C3-hydroxyacid may be obtained from the C3-oxygenate in a variety of ways. In FIG. 1, a number of preparation routes starting from C3-oxygenates and resulting in a C3-hydroxyacid are shown.

For a list of C3-oxygenates which may suitably be used in the present process wherein a C3-hydroxyacid is an intermediate, reference is made to the above lists of C3-oxygenates containing 1, 2 or 3 oxygen atoms. Preferably, the C3-oxygenate contains 2 or 3 oxygen atoms, such as the C3-oxygenates as shown in FIG. 1 (excluding the C3-hydroxyacids), more preferably monopropylene glycol. More preferably, the C3-oxygenate contains 2 oxygen atoms. Most preferably, the C3-oxygenate is monopropylene glycol.

Preferably, in the present process, the C3-oxygenate comprises a C3-diol and/or a C3-hydroxycarbonyl, in which case the process comprises:

converting the C3-diol and/or the C3-hydroxycarbonyl into a C3-hydroxyacid; and

converting the C3-hydroxyacid into acrylic acid.

Said C3-diol contains 3 carbon atoms and 2 oxygen atoms in the form of 2 hydroxyl groups. Said C3-hydroxycarbonyl contains 3 carbon atoms and 2 oxygen atoms in the form of a hydroxyl group and a carbonyl group. The other atoms in such C3-diol and C3-hydroxycarbonyl are hydrogen atoms. In the

present process, said C3-diol is preferably monopropylene glycol. Said C3-hydroxycarbonyl may be monohydroxyacetone or 2-hydroxypropanal. Preferably, said C3-hydroxycarbonyl is a mixture of monohydroxyacetone and 2-hydroxypropanal.

In the present process, the C3-oxygenate may be a C3-diol, preferably monopropylene glycol, in which case the process comprises:

converting the C3-diol into a C3-hydroxyacid, preferably lactic acid; and

converting the C3-hydroxyacid into acrylic acid.

One C3-diol or a mixture of two or more different C3-diols may be used in the present process. In a case where two or more different C3-diols are used, preferably, a mixture of a 1,2-diol (monopropylene glycol) and a 1,3-diol (1,3-dihydroxypropane) is used. Both said C3-diols may advantageously be converted into 2-hydroxypropanoic acid and 3-hydroxypropanoic acid, respectively, in a single oxidation step without prior separation of the 1,3-diols. The resulting mixture of C3-hydroxyacids may then be separated before dehydration. Alternatively, such mixture of C3-hydroxyacids may be converted into acrylic acid in a single dehydration step or in two consecutive dehydration steps without separation.

Further, in the present process, the C3-oxygenate may be a C3-hydroxycarbonyl, preferably a mixture of monohydroxyacetone and 2-hydroxypropanal, in which case the process comprises:

converting the C3-hydroxycarbonyl into a C3-hydroxyacid, preferably lactic acid; and

converting the C3-hydroxyacid into acrylic acid.

One C3-hydroxycarbonyl or a mixture of two or more different C3-hydroxycarbonyls may be used in the present process. In a case where two or more different C3-hydroxycarbonyls are used, preferably, a mixture of monohydroxyacetone, 2-hydroxypropanal and 3-hydroxypropanal, more preferably without 3-hydroxypropanal, is used. Said C3-hydroxycarbonyls may advantageously be converted into 2- and optionally 3-hydroxypropanoic acid in a single oxidation step without prior separation of the C3-hydroxycarbonyls. In a case where 3-hydroxypropanal is also part of said mixture, the resulting mixture of C3-hydroxyacids may then be separated before dehydration. Alternatively, such mixture of C3-hydroxyacids may be converted into acrylic acid in a single dehydration step.

Still further, in the present process, any mixture of one or more C3-diols and one or more C3-hydroxycarbonyls may be used. In such case, said mixture may advantageously be converted into 2- and/or 3-hydroxypropanoic acid in a single oxidation step without prior separation of the C3-hydroxycarbonyls. Further reference is made to the above two cases wherein either a mixture of two or more different C3-diols is used or a mixture of two or more different C3-hydroxycarbonyls is used.

The reactions from the preparation routes in FIG. 1 may be carried out in ways as will be exemplified hereinbelow. The ways in which these reactions may be carried out are not essential to obtaining the above-discussed advantages of the present invention.

In FIG. 1, the designation " $-H_2$ " refers to dehydrogenation in general. Such dehydrogenation may be either an endothermic dehydrogenation or an exothermic oxidative dehydrogenation wherein oxygen is added and water is released or a hydrogen transfer reaction. Therefore, in FIG. 1, the designation " $-H_2$ " also covers " $+0.5 O_2/-H_2O$ " (i.e. exothermic oxidative dehydrogenation) and hydrogen trans-

fer, according to which H_2 is not released as H_2 or H_2O but as hydrogenated product such as alcohol (from a ketone) or alkane (from an olefin).

Further, in FIG. 1, the designation " $+0.5 O_2$ " refers to oxidation in general. In some cases such as the oxidation of aldehydes to carboxylic acids, the desired conversion may also be achieved by adding water and release of hydrogen. Therefore, in FIG. 1, the designation " $+0.5 O_2$ " may also cover " $+H_2O/-H_2$ ". The oxidation step may use oxidants such as H_2O_2 , N_2O , peracids and other known organic and inorganic oxidants as well as electrochemical oxidation.

In general, there are the following types of reactions:

- (1) reactions involving hydrogenation of a carbonyl group to a hydroxyl group;
- (2) reactions involving dehydrogenation of a hydroxyl group to a carbonyl group or dehydrogenation of a carbonyl group to an α,β -unsaturated carbonyl group;
- (3) reactions involving oxidation of an aldehyde group or a primary hydroxyl group to a carboxylic acid group;
- (4) reactions involving dehydration of alcohols optionally followed by keto-enol rearrangement (e.g. monopropylene glycol to propanal or glycerol to 3-hydroxypropanal) or by hydrogenation of the resulting double carbon-carbon bond (glycerol to monopropylene glycol);
- (5) reactions involving rearrangement of 2,3-dihydroxypropanal to lactic acid; and
- (6) reactions involving hydroxyl-carbonyl isomerisation.

Reactions involving hydrogenation of a carbonyl group to a hydroxyl group as mentioned above under (1), may be carried out at a relatively low temperature, for example below $200^\circ C.$, and a relatively high hydrogen pressure, for example higher than 10 bar. The catalyst may be a supported metal catalyst.

Reactions involving dehydrogenation of a hydroxyl group to a carbonyl group or dehydrogenation of a carbonyl group to an α,β -unsaturated carbonyl group as mentioned above under (2), may be carried out at a relatively high temperature, for example above $200^\circ C.$, and a relatively low hydrogen pressure, for example lower than 1 bar. The catalyst may be a supported metal catalyst.

Reactions involving oxidation of an aldehyde group or a primary hydroxyl group to a carboxylic acid group as mentioned above under (3), may be carried out in the liquid phase at a relatively low temperature, for example at or below $200^\circ C.$, in the presence of a base and an oxygen containing gas. The catalyst may be a supported metal catalyst, wherein the metal may be a noble metal, such as gold. Alternatively, it may be carried out in the gas phase at a relatively high temperature, for example of from 250 to $350^\circ C.$, in the presence of an oxygen containing gas. The catalyst may be a mixed oxide that may be partly reduced under the reaction conditions.

Reactions involving dehydration of alcohols as mentioned above under (4), may be carried out in the gas phase at a relatively high temperature, for example at or above $150^\circ C.$, suitably of from 150 to $400^\circ C.$, using a solid acid and/or base catalyst. A keto-enol rearrangement may occur spontaneously over such catalysts. For a hydrogenation of the double carbon-carbon bond, the acid/base catalyst may also contain some hydrogenation activity. Such hydrogenation reaction may be carried out at a relatively high hydrogen pressure, for example higher than 10 bar.

Reactions involving rearrangement of 2,3-dihydroxypropanal to lactic acid as mentioned above under (5), may be carried out in the liquid phase at a relatively low temperature, for example of from 100 to $200^\circ C.$, in the presence of an acid or base catalyst.

Reactions involving hydroxyl-carbonyl isomerisation as mentioned above under (6), may be carried out using any suitable catalyst at a relatively low temperature, for example higher than 100° C., and may even be carried in the absence of a catalyst at an elevated temperature.

In the table below, some publications are cited which disclose suitable reaction conditions for some of the reactions from the above general reaction scheme and from the reaction scheme in FIG. 1. The disclosures of these publications are incorporated herein by reference.

Reaction	Publication
lactic acid → acrylic acid	Ind. Eng. Chem. Res., 2010, 49, p. 9082-9087; ACS Catal., 2011, 1, p. 32-41; Catal. Rev., 2009, 51, 3, p. 293-324; U.S. Pat. No. 2,859,240; Ind. Eng. Chem. Res., 2010, 49, p. 9082-9087; ACS Catal., 2011, 1, p. 32-41
3-hydroxypropanoic acid → acrylic acid dihydroxyacetone → lactic acid	Green Chem., 2011, 13, p. 1624-1632; US20070219391 Chem. Eur. J., 2010, 16, p. 7368-7371; Green Chem., 2011, 13, p. 1175-1181; ChemSusChem, 2009, 2, p. 625-627
monopropylene glycol lactic acid	J. Catal., 1998, 176, p. 552-560

That which is claimed is:

1. A process for producing acrylic acid, comprising:
converting a C3-oxygenate into a C3-hydroxyacid,
wherein said C3-oxygenate is selected from the group

consisting of monopropylene glycol, monohydroxyacetone, and 2-hydroxypropanal; and
converting the C3-hydroxyacid into acrylic acid, wherein the C3-oxygenate originates from converting a renewable feedstock into the C3-oxygenate.

2. A process according to claim 1, wherein the C3-oxygenate is monopropylene glycol.

3. A process according to claim 1, wherein the renewable feedstock is a sugar source.

4. A process according to claim 1, wherein the C3-oxygenate is a C3-diol or C3-hydroxycarbonyl, comprising:
converting the C3-diol or C3-hydroxycarbonyl into a C3-hydroxyacid; and

converting the C3-hydroxyacid into acrylic acid.

5. A process according to claim 4, wherein the C3-oxygenate comprises monopropylene glycol, comprising:
converting the monopropylene glycol into a C3-hydroxyacid, and

converting the C3-hydroxyacid into acrylic acid.

6. A process according to claim 4, wherein the C3-oxygenate comprises a C3-hydroxycarbonyl, comprising:
converting the C3-hydroxycarbonyl into a C3-hydroxyacid; and

converting the C3-hydroxyacid into acrylic acid.

7. A process according to claim 6, wherein the C3-oxygenate is a mixture of monohydroxyacetone and 2-hydroxypropanal.

8. A process according to claim 1, wherein the C3-oxygenate is a mixture of monopropylene glycol and one or more C3-hydroxycarbonyls.

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